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Rapid increase of thermal expansion of alkali halides near melting point

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In this note an analysis of the results of Pathak & Vasavada (1970, 1972) on the thermal expansion of NaCl, KCl and LiF has been reported and an attempt is made to obtain the contribution of higher order anharmonic terms in the potential energy function. It is shown for the first time that the anharmonic contribution varies exponentially with temperature.

The analysis of the results of Pathak & Vasavada (1970, 1972) on the thermal expansion for NaCl, KCl and LiF shows that the plots of the volume expansion coefficient β ($\simeq 3\alpha$, α is linear expansion coefficient) against T are almost linear up to a certain temperature, say T_0 ($T_0 \simeq 825°K$ for NaCl and KCl and 900°K for LiF) and then deviate considerably from linearity at higher temperatures. T_0 is approximately the temperature corresponding to the knee to the electrical conductivity versus $1/T$ plot.

Pathak & Vasavada (1970, 1972) have tried to explain the rapid rise of thermal expansion at high temperatures as due to the creation of vacancies. Now the fractional equilibrium vacancy concentration $\Delta N/N$ is given by

$$\frac{\Delta N}{N} = \exp(S_f/K)\exp(-E_f/KT) \qquad (1)$$

where S_f and E_f are the entropy and energy of vacancy formation respectively. If the appropriate values of S_f and E_f are substituted in the above equation, it is found that the fractional vacancy concentration is of the order of 10^{-5}.

The assumption that the deviation of volume expansion coefficient β from linearity is entirely due to vacancies requires that the values of $\Delta N/N$ should be $\simeq 10^{-3}$. Thus the contribution of vacancies must be negligible.

It can therefore be concluded that the large deviation of the thermal expansion curve from linearity at high temperature is almost certainly an anharmonic effect. It is probably a higher order anharmonic effect because the effect cannot be explained in terms of quasiharmonic theory, even if allowance is made for the volume change of the crystals with temperature. Explicite consideration of the fourth and higher order terms in the potential energy is required.

In view of these arguments we can write

$$\int_{T_0}^{T} \Delta\beta dT = \left(\frac{\Delta V^{L+H}}{V_0} - \frac{\Delta V^{L}}{V_0}\right)_{m} = \left(\frac{\Delta V}{V_0}\right)_T^H \tag{2}$$

Here $\Delta\beta$ is the difference between the observed β and that obtained by extrapolating the linear part of the graph. V is the volume corresponding to the temperature T_0 at which the curve starts deviating from linearity. The superscripts L and H denote respectively the lower order and higher order anharmonic contributions. The values of $(\Delta V/V_0)_T^{L+H}$ and $(\Delta V/V_0)_T^{L}$ are obtained from the plots β against T given by Pathak & Vasavada (1970, 1972). The difference between them gives the anharmonic contribution $(\Delta V/V_0)$ due to higher order terms in the potential energy at various temperatures.

The plots of $\log(\Delta V/V_0)_T^H$ against $1/T$ for NaCl, KCl and LiF are shown in figure 1. It is seen that the higher order contributions $(\Delta V/V_0)_T^H$ vary exponentially with temperature and are given by a general equation of the form

$$\left(\frac{\Delta V}{V_0}\right)_T^H = a \exp\left(\frac{-b}{T}\right) \tag{3}$$

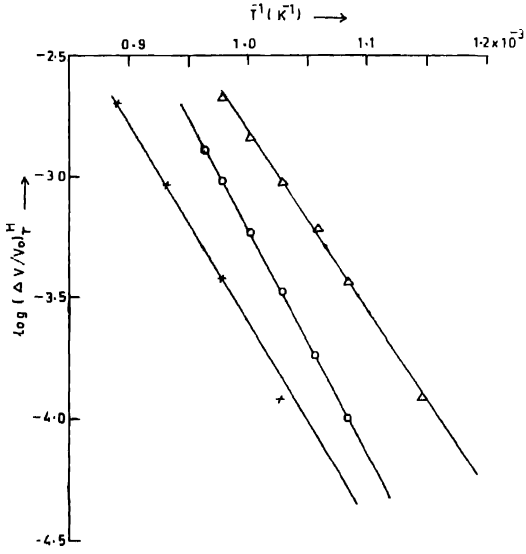

Fig. 1. Plot of logarithm of the anharmonic contribution against reciprocal of temperature for NaCl (O), KCl (Δ) and LiF (×).

The values of the constants a and b for the different alkali halides are given in table 1

Table 1 Values of the constants a and b for NaCl, KCl and LiF

Substance	a	b (°K)
NaCl	9.29×10^5	21.19×10^3
KCl	4.27×10^4	17.15×10^3
LiF	3.77×10^4	18.84×10^3

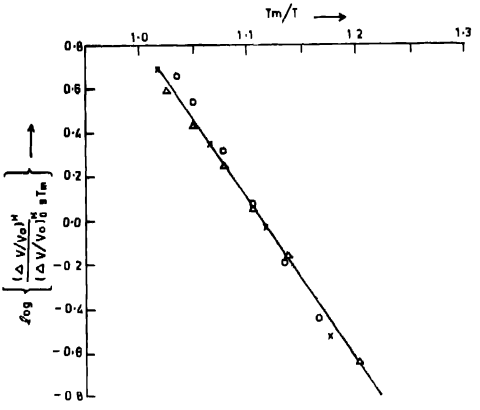

Fig. 2. Plot of $\log\{(\Delta V/V_0)^H / (\Delta V/V_0)_{0.9Tm}{}^H\}$ against Tm/T where Tm is the melting temperature. The symbols are O, NaCl; Δ, KCl; X, LiF

Figure 2 shows the plot of $\log\{(\Delta V/V_0)_T{}^H/(\Delta V/V_0)^H{}_{0.9Tm}\}$ against Tm/T, where Tm is the melting temperature. It is interesting to note that the points for the three halides considered fall on a common straight line whose equation is

$$\left(\frac{\Delta V}{V_0}\right)_T^H = 1{\cdot}48 \times 10^8 \left(\frac{\Delta V}{V}\right)_{0.9Tm}^H \exp\left(\frac{-16{\cdot}93\,Tm}{T}\right). \quad (4)$$

It is expected that this equation should apply to all alkali halides

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References

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